

Bridging function mediated intermetallic coupling in diruthenium-*bis*(bipyridine) complexes

SOMA CHAKRABORTY, BIPLAB MONDAL, BIPRAJIT SARKAR and GOUTAM KUMAR LAHIRI*

Department of Chemistry, Indian Institute of Technology – Bombay, Powai, Mumbai 400 076, India

e-mail: lahiri@ether.chem.iitb.ac.in

Abstract. The interactions of potentially dinucleating bridging functionalities (**I–VI**) with the ruthenium-*bis*(bipyridine) precursor $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{EtOH})_2]^{2+}$ have been explored. The bridging functions **I**, **II** and **VI** directly result in the expected dinuclear complexes of the type $[(\text{bpy})_2\text{Ru}^{\text{II}}\{\text{L}^z\}\text{Ru}^{\text{II}}(\text{bpy})_2]^{z+}$ (**1**, **2**, **7** and **8**) ($n = 0, z = 4$ and $n = -2, z = 2$). The bridging ligand **III** undergoes N–N or N–C bond cleavage reaction on coordination to the $\text{Ru}^{\text{II}}(\text{bpy})_2$ core which eventually yields a mononuclear complex of the type $[(\text{bpy})_2\text{Ru}^{\text{II}}(\text{L})]^+$, **3**, where $\text{L} = ^-\text{OC}_6\text{H}_3(\text{R})\text{C}(\text{R}')=\text{N}-\text{H}$. However, the electrogenerated mononuclear ruthenium(III) congener, **3**⁺ in acetonitrile dimerises to $[(\text{bpy})_2\text{Ru}^{\text{III}}\{\text{OC}_6\text{H}_3(\text{R})\text{C}(\text{R}')=\text{N}-\text{N}=(\text{R}')\text{C}(\text{R})\text{C}_6\text{H}_3\text{O}^-\}\text{Ru}^{\text{III}}(\text{bpy})_2]^{4+}$ (**4**). In the presence of a slight amount of water content in the acetonitrile solvent the dimeric species (**4**) reduces back to the starting ruthenium(II) monomer (**3**). The preformed bridging ligand **IV** undergoes multiple transformations on coordination to the $\text{Ru}(\text{bpy})_2$ core, such as hydrolysis of the imine groups of **IV** followed by intermolecular head-to-tail oxidative coupling of the resultant amino phenol moieties, which in turn results in a new class of dimeric complex of the type $[(\text{bpy})_2\text{Ru}^{\text{II}}\{\text{OC}_6\text{H}_4-\text{N}=\text{C}_6\text{H}_3(=\text{NH})\text{O}^-\}\text{Ru}^{\text{II}}(\text{bpy})_2]^{2+}$ (**5**). In **5**, the bridging ligand comprises of two *N,O* chelating binding sites each formally in the semiquinone level and there is a *p*-benzoquinonediimine bridge between the metal centres. In complex **6**, the preformed bridging ligand, 3,6-*bis*(3,5-dimethylpyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine, H_2L (**V**) undergoes oxidative dehydrogenation to aromatic tetrazine based bridging unit, 3,6-*bis*(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine, **L**. The detailed spectroelectrochemical aspects of the complexes have been studied in order to understand the role of the bridging units towards the intermetallic electronic coupling in the dinuclear complexes.

Keywords. Diruthenium complexes; metal-mediated transformations; intermetallic coupling; redox; spectroelectrochemistry.

1. Introduction

The development of newer classes of polynuclear ruthenium-polypyridine complexes incorporating suitable bridging functionalities are of considerable current research interest. This is primarily due to their potential use in diverse areas such as photosensitisers for photochemical conversion of solar energy¹, molecular electronic devices² and as photoactive DNA cleavage agents for therapeutic purposes³. The degree of electronic communication between the metal centres is essentially controlled by the electronic nature of the bridging units, which can mediate the electronic coupling through

*For correspondence

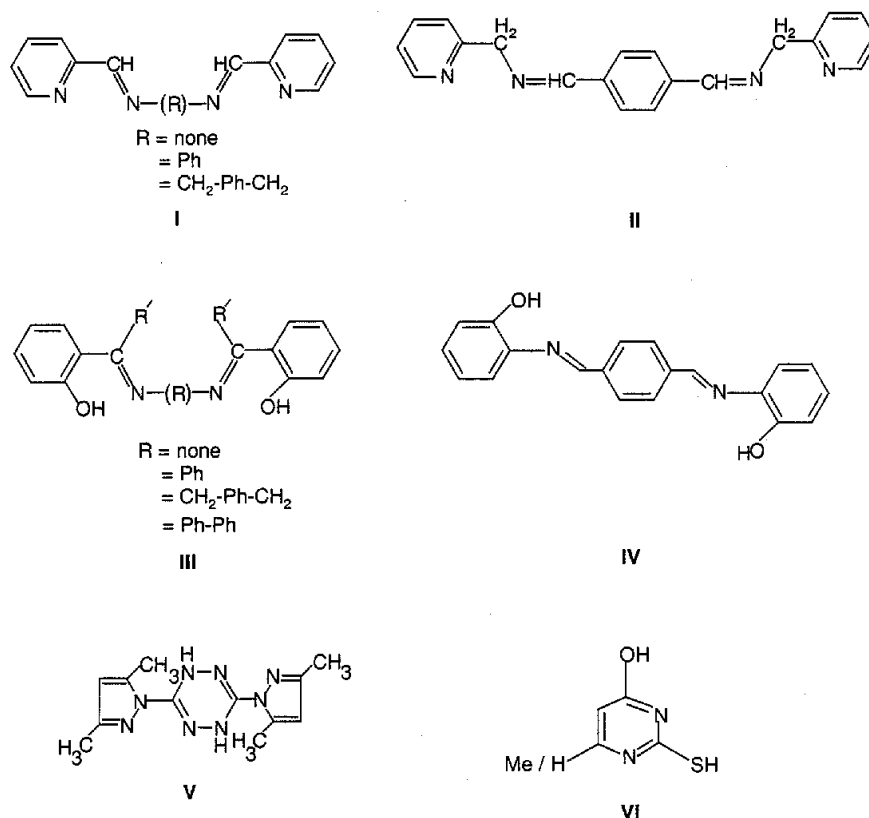
their *p* symmetry orbitals by either electron-transfer or hole-transfer mechanisms⁴. Bridging function mediated intermetallic electronic coupling is known to control the ground and excited state properties of such complexes.

In this context we have designed a group of new classes of diruthenium-*bis*(bipyridine) complexes incorporating neutral as well as anionic bridging functionalities and examined their spectroelectrochemical properties. Some of our recent observations are summarised in this note.

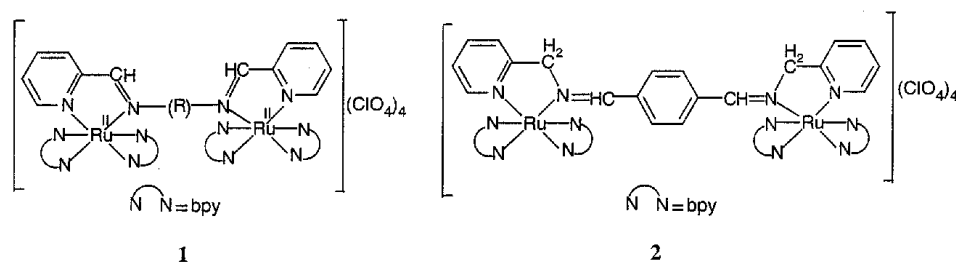
2. Results and discussion

The following neutral and anionic bridging ligands, **I–VI** (scheme 1) have been selectively chosen to synthesize diruthenium-*bis*(bipyridine) complexes of the type $[(bpy)_2Ru^{II}\{L^n\}Ru^{II}(bpy)_2]^{z+}$ ($n=0, z=4$ and $n=-2, z=2$). The bridging ligands (**I–VI**) essentially differ with respect to the electronic nature and charge associated with the donor centres.

The reactions of symmetric and neutral bridging ligands **I** and **II** with the ruthenium-bipyridine starting complex, $[Ru^{II}(bpy)_2(EtOH)_2]^{2+}$ in dry ethanol under dinitrogen atmosphere result in diruthenium complexes of the types **1** and **2**.



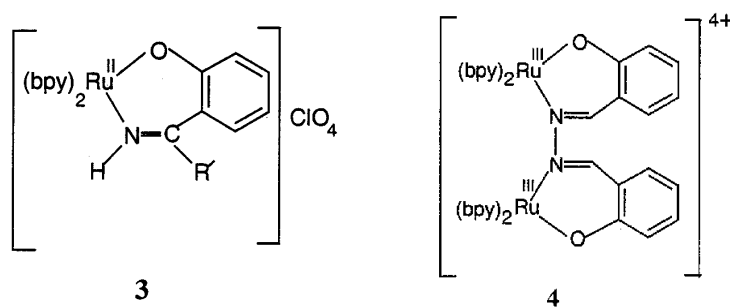
Scheme 1.



In acetonitrile solution the complex **1** exhibits one two-electron oxidation process near 1.5V vs SCE corresponding to the simultaneous oxidations of the two ruthenium(II) centres in **1**⁵. The appearance of simultaneous oxidations of both the metal centres across the bridging unit (**I**) implies a situation of typical class I type dinuclear species where there is existence of no or very weak intermetallic coupling^{2,5}.

In case of complex **2**, the two ruthenium(II) centres are found to undergo stepwise one-electron reversible Ru(II)/Ru(III) oxidations at 1.10V and 1.35V vs SCE in acetonitrile. Here the two Ru(II)/Ru(III) couples are separated by 225 mV (ΔE)⁶, which leads to the comproportionation constant (K_c) for the equilibrium process $\text{Ru}^{\text{II}}\text{Ru}^{\text{II}} + \text{Ru}^{\text{III}}\text{Ru}^{\text{III}} \rightleftharpoons 2\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$, 1.7×10^4 [K_c is obtained from the relation $RT \ln K_c = nF(\Delta E)$ where ΔE is the separation between the two Ru^{II}/Ru^{III} couples⁷]. The observed K_c value of 1.7×10^4 suggests that in **2**⁺ the metal centres are electronically moderately coupled through the bridging unit **II**, as is expected from a class II system. Consequently, the electrochemically generated mixed-valence Ru^{II}Ru^{III} species (**2**⁺) (258K, dichloromethane) displays a rhombic EPR spectrum at 77 K ($g_1 = 2.025$, $g_2 = 2.011$ and $g_3 = 1.906$)⁶, which reflects the valence-trapped Ru^{II}Ru^{III} configuration of the mixed-valence state (**2**⁺).

The reactions of diimine based dianionic bridging functions (**III**) with $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{EtOH})_2]^{2+}$ in presence of CH_3COONa result in monomeric complexes of the type **3**⁸. During the course of the reaction the N–N or N–C bond of the dinucleating bridging ligand (**III**) has been selectively cleaved, which eventually results in coordinated stable imine function incorporating the unusual –C(R)=N–H fragment. The formation of **3** has been authenticated by the crystal structures of two derivatives (R' = H and Me). Although **3** is stable enough both in the solid and solution states, electrochemically generated ruthenium(III) congener (**3**⁺) in dry acetonitrile slowly dimerises to the dimeric Ru^{III}Ru^{III} species, **4**. However, in presence of a slight amount of water content in the acetonitrile the dimeric species (**4**) as well as **3**⁺ reduce back to the initial monomeric ruthenium(II) complex **3**. The second order rate constant (k) of the conversion process

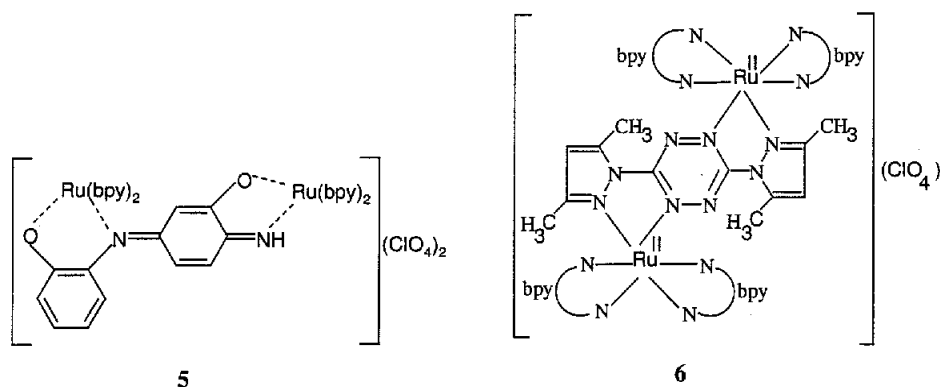


$3^+ \rightarrow 4$ in dry acetonitrile and the first-order rate constant (k') of $4 \rightarrow 3$ in ordinary acetonitrile and the activation parameters (ΔH^\ddagger and ΔS^\ddagger) of both the processes have been determined in the temperature range 303–333 K.

The dinucleating dianionic bridging ligand **IV** yields a new class of diruthenium-*bis*(bipyridine) complex **5**. In **5**, the hydrolysis of the imine groups of **IV** followed by intermolecular head-to-tail oxidative coupling of the resultant aminophenol fragments lead to the formation of a new N–C bond⁹. The crystal structures of **IV** and the complex, **5** have been determined. The structural parameters in combination with the spectro-electrochemical results indicate that in **5** the two nonequivalent *o*-iminophenol moieties are in semiquinone oxidation state and there is a *p*-benzoquinonediimine bridge between the two ruthenium centres.

It may be noted that under identical reaction conditions but in absence of **IV** the free *o*-amino phenol ligand fails to afford the complex **5**, which indicates the strong possibility of initial coordination of **IV** to the $\text{Ru}(\text{bpy})_2$ cores prior to the transformation processes.

The bridging ligand in $[(\text{bpy})_2\text{Ru}^{\text{II}}\{\text{L}^{\text{sq},\text{sq}}\}\text{Ru}^{\text{II}}(\text{bpy})_2]^{2+}$ (**5**) (sq = semiquinone oxidation state) undergoes two successive reversible one-electron oxidations in acetonitrile (0.12 and 0.35V vs SCE) to $[(\text{bpy})_2\text{Ru}^{\text{II}}\{\text{L}^{\text{q},\text{q}}\}\text{Ru}^{\text{II}}(\text{bpy})_2]^{4+}$ ($\mathbf{5}^{2+}$) (q = quinone oxidation state). The electrogenerated one-electron paramagnetic intermediate species $[(\text{bpy})_2\text{Ru}^{\text{II}}\{\text{L}^{\text{sq},\text{q}}\}\text{Ru}^{\text{II}}(\text{bpy})_2]^{3+}$ ($\mathbf{5}^+$) exhibits weakly rhombic EPR spectrum ($g_1 = 2.096$, $g_2 = 2.015$, $g_3 = 1.972$ in CH_2Cl_2 at 77 K), implying that the unpaired electron in $\mathbf{5}^+$ is primarily localised onto the ligand centre ($\text{L}^{\text{sq},\text{q}}$) with a small amount of unpaired spin-density on the ruthenium centre¹⁰. The bridging ligand ($\text{L}^{\text{sq},\text{sq}}$) in **5** successively reduces to $[(\text{bpy})_2\text{Ru}^{\text{II}}\{\text{L}^{\text{sq},\text{cat}}\}\text{Ru}^{\text{II}}(\text{bpy})_2]^+$ ($\mathbf{5}^-$) and then $[(\text{bpy})_2\text{Ru}^{\text{II}}\{\text{L}^{\text{cat},\text{cat}}\}\text{Ru}^{\text{II}}(\text{bpy})_2]$ ($\mathbf{5}^{2-}$) at -0.98V and -1.38V respectively. Moreover, successive irreversible $\text{Ru}(\text{II})/\text{Ru}(\text{III})$ oxidation processes are observed at 1.49 and 1.70V which correspond to the $K_c = 8 \times 10^3$, implying a moderately coupled class II species.

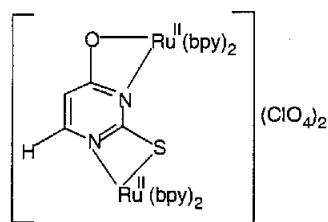


The initial sq,sq complex (**5**) exhibits $\text{Ru}(\text{II}) \rightarrow \text{L}^{\text{sq},\text{sq}}$ and $\text{Ru}(\text{II}) \rightarrow \text{bpy}$ MLCT transitions at 860 nm and 525 nm respectively. However, the 860 nm band corresponding to the $\text{Ru}(\text{II}) \rightarrow \text{L}^{\text{sq},\text{sq}}$ transition has been splitted into two closely-spaced components, at 892 and 984 nm on electrochemical one-electron oxidation to asymmetric bridging centre (sq,q) in $\mathbf{5}^+$. The intra-ligand charge transfer transition between the semiquinone and quinone termini in $\mathbf{5}^+$ has been observed at 1570 nm which however, disappears on further oxidation to symmetric q,q species ($\mathbf{5}^{2+}$). On one-electron reduction to $\mathbf{5}^-$ (sq,cat

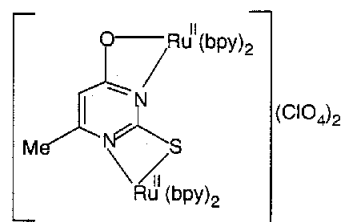
species) the lowest energy MLCT transition has been shifted to 1306 nm corresponding to the Ru(II) \rightarrow SOMO {L(cat,sq)} MLCT transition. Further, on one-electron reduction to cat,cat state ($\mathbf{5}^{2-}$), the 1306 nm transition disappears as the vacancy in the SOMO is filled and consequently Ru(II) \rightarrow bpy transition at 539 nm becomes the lowest energy MLCT transition.

The reaction of potentially binucleating neutral bridging ligand, 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine, H_2L (**V**) with $[\text{Ru}(\text{bpy})_2(\text{EtOH})_2]^{2+}$ produces a diruthenium complex of the type $[(\text{bpy})_2\text{Ru}^{\text{II}}(\text{L})\text{Ru}^{\text{II}}(\text{bpy})_2]^{4+}$, **6**¹¹. Although the preformed H_2L is stable enough both in the solid and solution states and requires treatment with strong chemical oxidants to be converted to L^{12} , during the course of the metallation process H_2L undergoes facile oxidative dehydrogenation to give one aromatic tetrazine unit (L) in **6**. The crystal structures of the free ligand (H_2L) and the complex **6** have been determined. The complex **6** exhibits two reversible Ru(II)/Ru(III) couples at 1.25 and 1.70V vs SCE, corresponding to the $K_c = 4 \times 10^7$. The tetrazine based two one-electron reversible reductions are observed at -0.13 and -0.99V vs SCE. The electrochemically generated one-electron reduced species shows an EPR signal at $g = 2.0085$ with a peak-peak separation of 45 G with some poorly resolved fine structures due to hyperfine coupling to the N-atoms, indicative of a largely tz-centred radical¹³. The Ru(II) \rightarrow (\mathbf{p}^*)L and Ru(II) \rightarrow (\mathbf{p}^*)bpy based MLCT transitions are observed at 757 nm and 400 nm respectively. For the mixed-valence $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$ complex (**6**⁺) the Ru(II) \rightarrow (\mathbf{p}^*)L transition is blue shifted to 633 nm and one sharp and intense $\mathbf{p}\mathbf{p}^*$ type transition has been observed at 1534 nm with a band width at half height, $\Delta\mathbf{n}_{1/2} = 650 \text{ cm}^{-1}$ and the electronic coupling parameter, $V_{ab} = 3260 \text{ cm}^{-1}$, characteristics of a strongly coupled class III species¹⁴. On further oxidation to **6**²⁺ ($\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}$ configuration) the remaining ruthenium(II) based MLCT transitions and the $\mathbf{p}\mathbf{p}^*$ transition are replaced by ligand \rightarrow Ru(III) LMCT transition at 522 nm.

The asymmetric bridging ligands 2-thiouracil (H_2L^1) and 6-methyl-2-thiouracil (H_2L^2), **VI** yield dinuclear complexes of the type $[(\text{bpy})_2\text{Ru}]_2(\mathbf{m}\mathbf{L}^{2-})]^{2+}$, where $\text{L} = \text{L}^1$ (complex **7**) or L^2 (complex **8**) in which the bridging functions act as a dinegative unit and bind with the two $[\text{Ru}(\text{bpy})_2]^{2+}$ units through the terminal N, S and N, O donor sites¹⁵. The crystal structure of **8** has been determined, which suggests that one negative charge is associated with each binding site i.e. L behaves like a combination of pyridonate and thiopyridonate ligands¹⁶. The stepwise one-electron Ru(II)/Ru(III) couples for **7** appear at half-wave potentials 0.17 and 0.87V vs SCE. The large separation of 700 mV between the successive Ru(II)/Ru(III) couples arises presumably due to the combination of the inherent difference in redox potentials associated with the chemically different sites at the bridging termini and an electronic interaction between the metal centres mediated by the



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8

p orbitals of the bridging ligand. The successive Ru(II)/Ru(III) couples for **8** appear at 0.41 and 0.72V with a separation of 310 mV. Both the complexes display a third oxidation process in the range 1.54–1.6V vs SCE, which is believed to be a process involving the thiolato unit of the bridging ligand¹⁷. The large decrease in separation of potentials of the successive Ru(II)/Ru(III) couples while moving from **7** (700 mV) to **8** (310 mV) possibly develops due to the steric hindrance associated with the presence of the methyl group on the bridging ligand (L^2) of **8**. This has been clearly reflected in the crystal structure of **8** where the adjacent Ru–N bond at the RuN₅S site is elongated. The mixed valence Ru^{II}Ru^{III} species [**7**]⁺ and [**8**]⁺ display a broad intervalence charge-transfer transition (IVCT) at 1160 nm and 1140 nm respectively. The widths at half height for these IVCT transitions are 3060 and 2400 cm⁻¹ and electronic coupling constant, V_{ab} of 950 cm⁻¹ for [**7**]⁺ and 900 cm⁻¹ for [**8**]⁺ respectively, which are characteristics of moderately coupled class II complexes¹⁸. The fractionally weaker coupling in [**8**]⁺ may be a reflection of elongated Ru–N bond to the bridging ligand which also resulted in a reduced separation between the redox potentials.

3. Conclusions

The present discussion primarily illustrates the following three important aspects: (i) the role of Ru(bpy)₂ core in facilitating the selective organic transformations of the coordinated bridging functions in the complexes **3**, **4**, **5** and **6**, (ii) the role of electronic nature of the bridging units in mediating the electronic coupling between the metal centres across the bridges in the mixed valent dinuclear species **1**⁺, **2**⁺, **5**⁺, **6**⁺ and **7**⁺, and (iii) the steric effect of the methyl substituent associated with the bridging function in **8** with specific reference to the intermetallic electronic coupling.

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